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Understanding the hydrogeology and surface flow in the Cuatrociénegas Basin (NE Mexico) using stable isotopes

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Nicholas Felstead – participated in field sampling for isotopic analysis, interpretation of data and is lead contributor to the article and its preparation, including all figures and tables.

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Abstract

In this paper we present surface water oxygen ($\delta^{18}O$), hydrogen (δD) and inorganic carbon ($\delta^{13}C_{DIC}$) isotope data to gain a better understanding of the modern day hydrogeology of Cuatrociénegas Basin, a semi-arid region in northeastern Mexico. Our study focuses on 26 water samples collected in March 2008 to investigate: 1) current provenance and flow pathways of surface waters, 2) the use of stable isotopes in identifying water loss and environmental degradation, and 3) human influence on hydrogeology. $\delta^{18}O$ for Cuatrociénegas water samples ranged from –7.99 to +4.97‰ (mean –5.23± 3.13‰), δD from –54.8 to +0.3‰ (mean –42.4 ± 14.4‰), and $\delta^{13}C_{TDIC}$ from –21.6 to –9.2‰ (mean –14.3 ± 3.4‰). Samples collected progressively away from their respective spring lines display increasing $\delta^{18}O$ and δD values. Isotope data suggest that where the residence time of the groundwater is long and/or the system is hydrologically open, $\delta^{18}O$ may not be a reliable indicator of water loss and environmental degradation. Our data suggest the central ciénega (area W(b)) is the most viable area for palaeoenvironmental study and long term monitoring is an essential tool in the identification of ecosystem damage and response, allowing for better future management of the complex and fragile CCB ecosystem.

Keywords: Groundwater; Chihuahuan Desert; Semiarid regions; Mexico

1. Introduction

Groundwater is the primary water resource in arid/semi-arid zones and it is well established that groundwater flow systems are vital to allowing human populations and other biota to survive (Ragab and Prudhomme, 2002; Hibbs and Darling, 2005; Scanlon *et al*. 2006; Herczeg and Leaney, 2011). Such spring fed ecosystems can give rise to endemic species of flora and fauna (Crowley and Ivanstoff, 1990; Deacon and Williams, 1991) that can be very fragile. Evaporation from soil in the unsaturated zone and surface waters remain the most influential processes that affect the oxygen isotope ($\delta^{18}O$) and deuterium isotope (δD) composition of surface water. If, for example, two or more lakes are joined, evaporative enrichment of $\delta^{18}O$ and δD in the lake waters increases with distance from the feeder spring (Clark and Fritz, 1997). Tracing the isotopic enrichment of water can be a good indicator of lake water balance and environmental degradation (Allison and Barnes, 1985; Gibson *et al*., 2002). Understanding the current day hydrogeology of a study region is an important aspect in palaeoenvironmental studies, elucidating the response of lake and wetland systems to past and future climate changes (Johnson *et al*. 1991; Dean *et al*. 2013).

The Cuatrociénegas Basin (CCB) situated in the Chihuahuan Desert region of Coahuila State, NE Mexico (26°N, 102°W) (Fig. 1) is a spring-fed system, and alongside Ash Meadows, Nevada, USA, is one of only two remaining fragile desert wetland ecosystems in North America (Deacon and Williams, 1991; Minckley, 1992). In this paper we aim to better understand the hydrogeology of the Cuatrociénegas Basin and to identify viable areas for palaeoenvironmental studies. We use isotope data for three main objectives to investigate: 1) the current provenance and flow pathways of surface waters, 2) the use of stable isotopes in identifying water loss and environmental degradation, and 3) the human influence on hydrogeology.

1.1. Study area

Lying within the steeply folded Cretaceous limestone ridges of the Sierra Madre Oriental, reaching >3000 m elevation, the CCB is a sedimentary basin with a surface area of 1400 km^2 and average valley-floor-elevation of 740 m above sea level (m a.s.l). Precipitation in the CCB is predominantly (~70%) during the summer wet season (May-Oct) with moisture originating in the Gulf of Mexico, the remaining ~30% is attributed to winter cold fronts (‘*nortes*’) during the winter dry season (Nov-Apr) (Metcalfe, 2006; Diaz *et al*., 2002; Villanueva-Diaz *et al*., 2007). Classified as semiarid (Schmidt, 1986), mean annual precipitation is ≤200 mm, falling mostly in September, whereas mean evaporation is > 2000 mm/yr (Johannesson *et al*. 2004). Average daily temperatures range from +6.3°C to +24.6°C, with highs of up to +40°C in July and August and lows of 0°C in December and January (Badino *et al*. 2004).

Established as an “Área de Protección de Flora y Fauna” in 1994 (SEMARNAP, 1996), the CCB has the highest endemic biodiversity in North America (Stein *et al*. 2000), and is home to over 70 species of endemic flora and fauna (Minckley, 1969; Hendrickson *et al*. 2008). The CCB has a diverse range of vegetation controlled by altitude. Pine-oak-juniper woodlands are found on the highest peaks (>2000 m a.s.l), whilst on the valley floor (<800 m a.s.l) halophilous species such as Chenopods occur alongside xerophytes (Asteraceae) and desert succulents such as prickly pear cacti (Quintanilla, 2001).

Figure 1

1.2. Hydrogeology

Groundwater discharge into CCB is thought to be from prominent N-S faulting of the Sierra San Marcos (Fig. 2), with fractures that penetrate the regional Cupido-Aurora carbonate aquifer of northeastern Mexico (Lesser and Lesser, 1988; Lehmann *et al*. 1999; Wolaver *et al*., 2013). The early conceptual flow models suggested the dominant groundwater flow through the Cupido-Aurora aquifer is in an easterly direction, towards the Gulf coastal plain region, after recharging in the high Sierra Madre Oriental mountain range (Lesser and Lesser, 1988). However, subsequent studies elucidate more complex regional hydrogeology; in particular, there is the likelihood of additional recharge from farther afield to the north, south and west, that all contribute to observed discharge in the CCB (Johannesson *et al*.2004; Evans, 2005; Rodriguez *et al*., 2005; Wolaver *et al*., 2008; Fig. 1).

Over 200 springs, seeps, ponds, pools (*pozas*), lakes (*lagunas*) and rivers (*rios*) are documented in the CCB (Minckley and Cole, 1968; Minckley, 1969; Minckley, 1992; Badino *et al*. 2004). Previous geochemical studies suggest that waters issuing along the western springline of the Sierra San Marcos are consistent with fluids associated with the Cupido-Aurora aquifer (Wolaver *et al*., 2013), with evidence of evaporative through-flow between water bodies (Johannesson *et al*., 2004). Waters issuing along the eastern springline of the Sierra San Marcos are thought to be a mixture of Cupido-Aurora aquifer and local mountain recharge water (Wolaver *et al*., 2013), with isolated spring systems associated with local mountain recharge at the base of Sierras La Purisma (Rodriguez *et al*., 2005) and La Madera (Johannesson *et al*., 2004; Rodriguez *et al*., 2005). The majority of the water bodies flow through marsh areas (*ciénegas*), however some pools are marginal endorheic or seasonally ephemeral, although these are most commonly found in the central eastern area of the basin (Minckley, 1969; Badino *et al*. 2004; Evans, 2005).

1.3. Human activity and groundwater impact

Extraction of surface and groundwater within the CCB for agricultural irrigation, sanitation and drinking has been in operation since the early 1900s (Minckley, 1969), in particular through canals such as the Saca Salada (1902, 80 km, ~970 l/s), the Becerra (1966, 25 km, ~580 l/s), and the Santa Tecla (1966, 53 km, ~200 l/s) (Fig. 2). Since the 1960s, human water exploitation within the CCB has intensified with a three-fold increase in irrigated agriculture (Minckley, 1992), with canal outflow discharge currently estimated to be approximately 5.3 x $10^7 m^3$/yr (Wolaver *et al*. 2008). In addition to this, large scale groundwater pumping of 7.7 x 10^7 m^3/yr (Lesser, 2001) for irrigation of c. 4,000 hectares of pastureland, occurs in the neighbouring Ocampo and Hundido basins, north and west respectively (Fig. 1). The extraction of a combined 1.3 x 10^8 m^3/yr of groundwater from the region is thought to have contributed to water level declines throughout the CCB in the past 40 years, and caused the complete drying up of Laguna Grande (Fig. 2) in 2009 according to the Comisión Nacional de Áreas Naturales Protegidas (CONANP) (CONANP, pers. comm., January 2010). Recent estimates also indicate a ~1m/yr drop in the water table levels of the surrounding basins since extraction began (Wolaver *et al*. 2013).

Estimates of spring discharge in the CCB are basic (calculations are based on discharge from 1-2 water sources) but are lower than those of regional extraction, ranging from approximately 3.5 x $10^7 m^3$/yr to 1.26 x 10^8 m^3/yr (Johannesson *et al*., 2004; Wolaver *et al*., 2008). This is compounded by basin wide potential evapotranspiration (PET) in the region of 2.8 x 10^9 m^3/yr, or 2000 mm/yr (Johannesson *et al*. 2004). Modern PET being an order of magnitude higher than spring discharge alone suggests a significant component of CCB groundwater is as of yet unaccounted for, highlighting the importance of greater understanding of the CCB hydrogeology.

Figure 2

2. Methods

Water samples were collected for $\delta^{18}O$, δD and $\delta^{13}C_{TDIC}$ analysis in March 2008 (dry season) from 15 pools, 3 springs, 2 lakes, 2 rivers, 2 streams, and 2 salt pools (Fig. 2). Water samples were collected using 250 ml polyethylene terephthalate plastic bottles from the epilimnion (>30 cm below the air-water interface). Wet season samples were not collected as we were not able to conduct a summer field season, although it is assumed wet season flooding events would lead to lower isotope ratios (‘amount effect’) (Clark and Fritz, 1997). Due to equipment failure during the sampling, we were unable to collect water temperature data. Where published temperature data are not available, qualitative assessments of water body temperature ranges were made on-site in conjunction with CONANP rangers. Therefore, temperature data are presented as three range categories: hot (>26°C), ambient (20-25°C) and cool (<20°C). Although, where possible, published water temperature data have been used to categorise the water temperatures (i.e. Badino *et al*. 2004; Johannesson *et al*. 2004). For full analytical methodology please see online supplementary materials.

Table 1: Summary of sampled sub-regions in the Cuatrociénegas Basin.

Sampling sub-region (Fig. 2)	**Hypothesised flow systems**	**Sub-region description**
Area W(a)	Churince system (Minckley, 1969; Evans, 2005)	A mixture of hot pools and a cool lake (Laguna Grande) in close proximity to the fault zone of the Sierra San Marcos, the main discharge zone of the Cupido-Aurora aquifer in the CCB (Johannesson *et al*. 2004; Wolaver *et al*. 2013)
Area W(b)	Garabatal-Becerra-Rio Mesquites system (Minckley, 1969; Evans, 2005) Anteojo system (Evans, 2005)	A mixture of hot pools, ambient pools and rivers, and cool pools centred around the ciénega (marsh) area of the piedmont of the Sierra San Marcos y Pinos, an important archaeological area of the CCB (Gonzalez *et al*. 2007; Felstead *et al*. 2014)
Area E(a)	Tio Candido-Hundidos system (Evans, 2005; Wolaver *et al*, 2006; 2013)	Cool pools close to the east of the Sierra San Marcos y Pinos (Poza Quintero, Poza Pronatura and Los Hundidos), a region associated with an eastern spring line (Wolaver *et al*. 2006; 2013).
Area E(b)	Las Playitas (Minckley, 1969)	Cool endorheic and seasonally ephemeral pools in the centre of the eastern basin of the CCB (Las Salinas and Charco Rojo)

Sampling was focused on waters issuing from the Sierras San Marcos and Madera due to these areas being most exploited through pumping and canalization (Minckley, 1992; Evans, 2005; Rodriguez *et al*., 2005). Four sub-regions (Areas Wa, Wb, Ea, Eb) were sampled to give an overall view of the CCB, focusing on both basin floor high and low points, prominent groundwater discharge zones and areas of socio-economic importance, and are summarized in Table 1. Waters issuing from the western springline (Fig. 2) and high discharge springs in the CCB support the wetland ecosystem located around the piedmont of the Sierra San Marcos, and are the same as those used to irrigate farms in the region (Wolaver *et al*. 2013). Thus, areas W(a) and (b) were of particular importance due to their proximity to the western springline of the

Sierra San Marcos and recent suggestions that these areas are most at risk of environmental degradation (Souza *et al*. 2012).

Table 2: Stable isotope values ($\delta^{18}O$, δD and $\delta^{13}C_{TDIC}$), temperature (°C) and location for samples taken in the CCB. $\delta^{18}O$ and δD are reported (as ‰) relative to the standard VSMOW. $\delta^{13}C_{TDIC}$ is reported (as ‰) relative to the standard VPDB. [a]Data from Johannesson *et al*. (2004). [b]Data from Badino *et al*. (2004).

Location	**Area/Code (Fig.2)**	**Date**	**Lat (N°)/Long (W°)**	**Temp (°C)**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**$\delta^{13}C_{TDIC}$ (‰)**
Poza Anteojo	W(b)/A	12/3/2008	26°58’04.58”/102°07’38.22”	26.2[a]	–7.99 –8.2[a]	–54.8 –52[a]	–15.7
Poza Churince	W(a)/PC	11/3/2008	26°50’24.76”/102°08’02.40”	32[b]	–6.92	–50.3	–19.8
San Marcos	W(a)/SM	11/3/2008	26°48’22.51”/102°09’23.08”	>26	–6.68	–49.6	…
Poza Becerra	W(a)/B	11/3/2008	26°52’42.98”/102°08’17.27”	32.4[a]	–6.63 –6.7[a]	–48.9 –48[a]	…
Laguna Churince	W(a)/LC	11/3/2008	26°50’54.00”/102°08’30.03”	>26	–5.71	–45.3	–15.1
Laguna Grande	W(a)/LG	11/3/2008	26°51’09.51”/102°09’05.15”	<20	+1.17	–10.0	–13.9
Poza Garabatal	W(b)/G	12/3/2008	26°53’42.71”/102°08’42.02”	18.6[a]	–6.58 –6.4[a]	–47.9 –46[a]	–17.6
Poza Azul	W(b)/Az	13/3/2008	26°55’21.41”/102°07’20.84”	31[b]	–6.51	–48.0	–13.2
Mex 30-1	W(b)/30-1	12/3/2008	26°53’42.65”/102°08’31.57”	20-25	–6.37	–48.7	–12.4
Poza Juan Santos	W(b)/JS	12/3/2008	26°53’52.00”/102°08’53.82”	26.7[a]	–6.35 –6.4[a]	–47.5 –46[a]	–11.1
Palm Spring	W(b)/PS	12/3/2008	26°54’27.71”/102°09’24.41”	<20	–6.34	–47.1	–9.2
Rio Mesquites	W(b)/RM1	13/3/2008	26°55’14.53”/102°08’21.31”	20-25	–6.27	–48.3	–21.6
Poza Azul II	W(b)/AzII	13/3/2008	26°55’47.60”/102°07’30.35”	20-25	–6.24	–47.1	–10.8
Poza Azul I	W(b)/Az I	13/3/2008	26°55’52.82”/102°07’28.28”	20-25	–6.16	–47.0	–14.7
Rio Mesquites 2	W(b)/RM2	12/3/2008	26°55’23.11”/102°07’06.48”	20-25	–6.14	–45.7	–11.8
Bone Site	W(b)/BS	12/3/2008	26°54’59.46”/102°07’19.13”	<20	–6.13	–46.3	–13.4
Fast Stream	W(b)/FS	13/3/2008	26°54’46.38”/102°09’41.42”	<20	–5.84	–45.3	–10.0
Yucca Pond	W(b)/YP	13/3/2008	26°54’45.89”/102°09’13.89”	<20	–5.79	–45.1	–10.2
Rim Pond	W(b)/RP	13/3/2008	26°54’38.16”/102°09’38.48”	<20	–5.75	–45.5	–18.8
Mex 30-2	W(b)/30-2	12/3/2008	26°54’19.04”/102°09’12.56”	20-25	–5.75	–45.2	–10.4
Poza Tierra Blanca	W(b)/TB	12/3/2008	26°54’38.24”/102°09’10.20”	<20	–5.68	–44.5	–18.0
Poza Quintero	E(a)/Q	13/3/2008	26°51’09.31”/102°03’09.70”	<20	–6.84	–50.1	–13.3
Poza Pronatura	E(a)/P	13/3/2008	26°51’47.53”/102°02’31.15”	<20	–6.80	–49.4	–16.2
Los Hundidos	E(a)/LH	14/3/2008	26°51’59.35”/102°01’54.77”	<20	–5.67	–44.0	–14.8
Las Salinas	E(b)/LS	14/3/2008	26°54’42.90”/102°00’50.64”	<20	+2.98	–2.0	–17.5
Charco Rojo	E(b)/CR	14/3/2008	26°54’53.40”/102°00’33.23”	<20	+4.97	+0.3	…

3. Results

3.1. Oxygen and hydrogen isotopes

$\delta^{18}O$ and δD data for the 26 locations (Fig. 2) in the CCB are presented in Table 2 and are plotted on Figure 3a alongside the Global Meteoric Water Line (GMLW, Craig, 1961) and Local Evaporation Lines (LEL) from the CCB (Johannesson *et al*. 2004; Rodriguez *et al*. 2005). $\delta^{18}O$ and δD values of seasonally weighted groundwater (indicative of precipitation values) in the CCB are –8.3‰ and –55.8‰ respectively (Wassenaar *et al*. 2009), although no meteoric water line is available for the CCB (Johannesson *et al*. 2004;). However, the Local Meteoric Water Line (LMWL) from Chihuahua (Cortés *et al*. 1997) is used here due to Chihuahua receiving precipitation from the same atmospheric moisture sources as the CCB: summer Gulf of Mexico monsoon and winter 'nortes' (Johannesson *et al*. 2004).

All of the isotope data from our samples plot to the right of the GMWL and the LMWL (Fig. 3a). Of the 26 samples, 22 of them are grouped together with $\delta^{18}O$ and δD values of the water ranging from –6.92‰ to –5.67‰ and –50.3‰ and –44‰ respectively. A linear regression line through the data (n = 26) (Fig. 3a) indicates a LEL defined by equation: $\delta D = 4.5\delta^{18}O–19$. The samples plot within the range reported for the CCB previously (Johannesson *et al*. 2004; Rodriguez *et al*., 2005) The slope of 4.5 is lower than that of both Johannesson *et al*. (2004) and Rodriguez *et al*. (2005), with slopes of 4.9 and 5.15 respectively.

The LEL shows a high linear correlation between $\delta^{18}O$ and δD ($R^2 = 0.99$) and extrapolation back to the LMWL gives a hypothetical meteoric water value of –8.4‰ and –57‰ for $\delta^{18}O$ and δD respectively.

Figure 3

3.1.1. Area W(a)

The five water samples in this sub-region range from –6.92‰ (Poza Churince) to +1.17‰ (Laguna Grande) and –50.3‰ and –10‰ for $\delta^{18}O$ and δD respectively. Laguna Grande appears to be anomalous as it is the only sample to display a positive $\delta^{18}O$ value in areas W(a), W(b) and E(a) and also the only sample with a temperature of <20°C in W(a).

3.1.2. Area W(b)

The 16 water samples in this sub-region range from –7.99‰ (Poza Anteojo) to –5.68‰ (Poza Tierra Blanca) and –54.8‰ to –44.5‰ for $\delta^{18}O$ and δD respectively. Poza Anteojo water plots very closely to the intersection of the GMWL and LMWL. The data indicate two flow paths through W(b): 1) waters showing $\delta^{18}O$ enrichment from –6.58‰ to –6.14‰ around the piedmont (PG, 30-1, JS, PS, 30-2, RMI, AzII, AzI, Az, RM2) (Fig. 2), and 2) low temperature waters showing $\delta^{18}O$ enrichment from –6.13‰ to –5.68‰ through the ciénega area (BS, FS, YP, RP, TB) (Fig. 2).

3.1.3. Area E(a)

There are three water samples in this sub-region, ranging from –6.84‰ (Poza Quintero) to –5.67‰ (Los Hundidos) and –50.1‰ to –44‰ for $\delta^{18}O$ and δD respectively. These three samples progressively enrich in ^{18}O towards area E(b) (Table 2, Figs. 2 and 3a).

3.1.4. Area E(b)

The two water samples in this sub-region (Las Salinas and Charco Rojo) both have positive $\delta^{18}O$ values of +2.98‰ and +4.97‰ respectively, and δD values of –2‰ and +0.3‰ respectively. Both areas W(b) and E(a) display $\delta^{18}O$ enrichment east towards area E(b) (Table 2, Figs. 2 and 3a).

3.2. Carbon isotopes

$\delta^{13}C_{TDIC}$ data for the 26 locations in the CCB are presented in Table 2 and are plotted against $\delta^{18}O$ in Figure 3b. Pozas San Marcos, Becerra and Charco Rojo did not contain sufficient amounts of bicarbonate for $\delta^{13}C_{TDIC}$. $\delta^{13}C_{TDIC}$ values range from –21.6‰ (Rio Mesquites 1) to –9.2‰ (Palm Spring).

4. Discussion

The GMWL is based on precipitation data from around the world (Craig, 1961). Deviations away from the GMWL, in the form of a LMWL or LEL, are comprised of a sample set of local sites, specific to one region. Extrapolation of these lines back to the intersection with the GMWL indicates the isotope composition of the precipitation source for that set of local sites (Clark and

Fritz, 1997). The intersection of the GMWL, LMWL and LEL at –8.4‰ ($\delta^{18}O$) and –57‰ (δD) (Fig. 3a) coincident with the isotope composition of seasonally weighted groundwater (Wassenaar *et al*. 2009) suggests a common precipitation source for the CCB regional groundwater. The position of our samples to the right of the GMWL and LMWL indicates that they have undergone varying degrees of evaporative enrichment, defining the LEL with a slope of 4.5 (Fig. 3a), this is consistent with Evans (2005) suggestion that evaporation is the main reason for water loss in the basin.

The main thermal springs in the CCB (Poza Anteojo and Becerra) have undergone least evaporation (Table 2) and are categorised as low evaporation end members (Evans, 2005). The $\delta^{18}O$ and δD values for Poza Anteojo (–7.99‰, –54.8‰) closely match seasonally weighted modern precipitation for the CCB (Wassenaar *et al*. 2009), whereas isotope values for Poza Becerra (–6.63‰, –48.9‰) are higher (Table 2) suggesting that Poza Anteojo water is sourced from groundwater different to that of systems arising from Sierra San Marcos groundwater, as suggested by Johannesson *et al*. (2004). Recharge elevation has been suggested as a reason for these differences (Johannesson *et al*. 2004; Rodriguez *et al*. 2005) with estimates in the region of –0.48‰/100 m for $\delta^{18}O$ (Rodriguez *et al*. 2005). However, residence times >60 yr (Wolaver *et al*. 2013) and the well mixed nature of the CCB groundwater indicated by adherence to the LEL (Fig. 3a) suggests that recharge elevation estimates may be inaccurate (Blasch and Bryson, 2007).

Karst flow is often not straightforward in the CCB (Evans, 2005; Piccini *et al*. 2007) although distinct flow systems for the CCB have been previously hypothesised (Minckley, 1969; Evans, 2005, Table 1). Based on our results and CCB topography, we suggest four hydrologic systems in the CCB: 1) A high water temperature system probably independent from the other aquifers e.g. Poza Anteojo; 2) High water temperature, but also an evaporative through-flow system discharging at the western base of the Sierra San Marcos y Pinos (Fig. 2); 3) A low water temperature, evaporative through-flow system discharging on the eastern base of the Sierra San Marcos y Pinos (Fig. 2); and 4) low water temperature endorheic system resulting from the termination of hydrologic systems 2 and 3. These systems are broadly consistent with previously hypothesised systems and are further discussed below:

4.1. Current provenance and surface flow pathways of CCB waters

4.1.1. Poza Anteojo system

Poza Anteojo in area W(b) (Fig. 2) could be sourced directly from the limestone karst system, arising from Sierra Madera, but the warm temperature of the water (26.2˚C reported by Johannesson *et al*. (2004)), is higher than the CCB average mean annual air temperature of 21.2˚C (Badino *et al*. 2004) suggesting that Poza Anteojo water has a component of deep thermal water (e.g. focused channel recharge (Blasch *et al*. 2008)). Tritium values reported by Wolaver *et al*. (2013) indicate a long residence time of >60 years for water at this site. This residence time along with low conductivity and high carbonate concentrations (Evans, 2005) suggests the Poza Anteojo system is independent from the regional groundwater system (Fig. 1) and might also explain the lack of response in $\delta^{18}O$ and δD to groundwater extraction between sampling in 1999 (Johannesson *et al*. 2004) and our sampling in 2008. The Sierra Madera karst reservoir feeding Poza Anteojo may form a part confined aquifer, with CCB specific recharge/discharge, heated by deep circulation, similar to arid groundwater recharge areas in Arizona and Texas (Kastning, 1983; Hogan *et al*. 2004; Blasch *et al*. 2008).

4.1.2. Churince-Garabatal-Becerra-Rio Mesquites (CGBRM) system

The prominent hydrologic feature in the CCB is an evaporative through-flow system originating to the west of the basin in area W(a) and flowing east through areas W(b) and E(b), based on evidence of progressive evaporation (Figs. 2 and 3a). Pozas Churince (PC) and Becerra (B) mark the beginning of the system, and their proximity to the western springline suggests waters issuing from these pools are from the Cupido-Aurora aquifer. Again, Wolaver *et al*. (2013) suggest groundwater of long residence time. Despite having similar isotopic values to both Pozas Churince and Becerra, Poza San Marcos (SM) does not appear to form part of the through-flow system, though it may be linked through sub-surface channels that are prevalent throughout the basin. The thermal waters on the west side of the CCB issue from local faulting (Badino *et al*. 2004; Johannesson *et al*. 2004; Evans, 2005), and are of a Ca-SO_4 type (Winsborough, 1990; Johannesson *et al*. 2004; Evans, 2005; Wolaver *et al*. 2013), resulting in gypsum deposition. If these thermal pools were recharged from the surrounding Cretaceous limestone ranges, we would expect the water to have higher $\delta^{18}O$ values (e.g. Poza Anteojo) and be of a Ca-HCO_3 type, as seen in waters issuing to the east of the Sierra San Marcos y Pinos (Evan, 2005), and more widely in the Sierra Madre Oriental (Rodriguez *et al*. 2005). Johannesson *et al.* (2004) note the presence of gypsum in the Sierra de la Fragua (see Fig. 2), so the SO_4-rich waters might originate there. These pools progressively become $\delta^{18}O$ enriched along the northern axis of the spring line through area W(a) (Figs. 2 and 3a). The Churince and Becerra systems have previously been hypothesised to be independent from each other (Minckley, 1969; Evans, 2005). However, surface mixing of waters between the pools (dictated by topography) and pools further north along the spring line which are at systematically lower elevations (Poza Churince 745 m a.s.l; Becerra 741 m a.s.l), and are progressively more evaporated, suggest these two systems are linked by surface and/or sub-surface channels.

As the Churince-Garbatal-Becerra-Rio Mesquites system reaches the piedmont of the Sierra San Marcos (Area W(b), Fig. 2) the flow pattern across the CCB becomes a complex mix of cold and ambient surface, ambient subterranean and thermal groundwater flow (Table 2; Figs. 2 and 3a) with significant subterranean exchanges between different flow processes, similar to those observed in ciénegas (marshes) of the Sonoran desert (Minckley and Brunelle, 2007; Minckley *et al*. 2009). This region of the basin is relatively sheltered from evaporation due to sub-surface channels and mixing of waters (Evans, 2005). The Rio Mesquites drains this area of the basin, flowing towards the terminal system in the east of the CCB (area E(b)), and it becomes hard to ascertain which water bodies mix at this point (Fig. 3a).

4.1.3. Tio Candido-Hundidos system

The Tio Candido-Hundidos system evident in the CCB originates on the east side of the Sierra San Marcos y Pinos at Poza de Quintero (Q) before flowing to Poza Pronatura (P) and towards Los Hundidos (LH) (Fig. 2). The water bodies plot on the LEL, similar to the main through-flow system in Figure 3a. Poza de Quintero ($\delta^{18}O$ –6.84‰) has a very similar isotopic composition to that of Pozas Churince and Becerra (Johannesson *et al*. 2004). However, unlike the hydrothermal water bodies sourced from the Cupido-Aurora aquifer on the western base of the Sierra San Marcos y Pinos, Poza Quintero is a cool water body (<20˚C) and there are no associated gypsum deposits, as with the Ca-SO_4 water issuing from the western spring line. This system may be sourced from local karst reservoir water, consistent with Ca-HCO_3 composition waters reported in previous studies (Minckley and Cole, 1968; Winsborough, 1990; Evans, 2005; Wolaver *et al*. 2006). Wolaver *et al*. (2013) record slightly higher tritium values at sites east of the Sierra San Marcos y Pinos consistent with more localised flow and shorter residence time, indicating a third groundwater source for the CCB and possibly a better irrigation abstraction area away from the fragile Churince-Garbatal-Becerra-Rio Mesquites system.

Alluvial fans at the eastern piedmont base of the Sierra San Marcos y Pinos may prevent the circulation of deep, thermal water and no faults are evident in the limestone strata to suggest any direct upwelling (Lesser and Lesser, 1988). It is worth noting that we did not sample further south on the eastern spring line, the origin point of the Santa Tecla Canal (Fig. 2). A limited number of hot water bodies e.g. Poza Escobedo, form on the eastern flank of the Sierra San Marcos through upwelling of hot water where alluvial fans are not located (Badino *et al*. 2004; Wolaver *et al*. 2008; 2013). The secondary through-flow system could also form part of a larger, eastern CCB flow system with greater numbers of water bodies, both hot (25˚C to 35˚C) and cool (<20˚C).

4.1.3. Endorheic system

The two pools – Las Salinas (LS) and Charco Rojo (CR) – forming this system, are very distinctive on Figure 3 and are highly evaporated. Known locally as Las Playitas (meaning little beaches or plains) because of the prevalence of trona and nahcolite evaporates (Badino *et al*. 2004), area E(b) is the lowest elevation (~700 m a. s. l) area in the CCB and where the Churince-Garbatal-Becerra-Rio Mesquites and Tio Candido-Hundidos systems terminate. Evans (2005) suggests that the precipitation of gypsum minerals in this region of the basin indicates some Ca-SO_4 waters may be flowing across the entirety of the CCB from the western springline, although we didn't observe any such deposits in our study.

4.1.4. Carbon isotopes

$\delta^{13}C_{TDIC}$ values range from –21.6‰ to –9.2‰ in the 23 measurable water samples in the CCB reflecting different soil and bedrock interactions. Water bodies with lower $\delta^{13}C_{TDIC}$ values, in the range of –22‰ to –16‰ (Table 2; Fig. 3b) probably indicate a greater input/interaction with soil carbon derived from plants and soils. Water bodies with higher $\delta^{13}C_{TDIC}$ values, in the range of –16‰ to –9‰ (Table 2; Fig 3b), more likely suggest a larger component of groundwater aquifer discharge or input of soil carbon from C_4 vegetation which have a higher $\delta^{13}C$ than C_3 plants. It is unlikely that the different degrees of evaporation have much effect on $\delta^{13}C$ since there is no relationship between $\delta^{18}O$ and $\delta^{13}C_{TDIC}$ (Fig. 3b).

All of the water bodies in the CCB contain a component of bicarbonate from the limestone aquifers. Bralower *et al*. (1999) estimate the Cupido-Aurora limestone to have $\delta^{13}C_{TDIC}$ values of +2‰ to +4.5‰ which indicates that dissolution of the Cupido-Aurora limestone would result in ^{13}C enriched groundwater. The high temperature Cupido-Aurora aquifer sourced water bodies in the CCB all have high $\delta^{13}C_{TDIC}$ values indicating that the carbon is from a mixture of soil CO_2, aquifer dissolution and endogenic sourced carbon (Wolaver *et al*. 2013).

With the limited data available, it is unclear what these compositional differences mean in terms of the hydrogeology of the basin, although they do highlight the very complex nature and histories of the CCB waters.

4.2. Water loss, environmental degradation and human impact

Observed drought and drying of water bodies within the CCB during the period between studies (1999 to 2008) (CONANP, pers. comm. 2010) suggest that PET is increasing and there are compounding problems associated with pumping and large scale water extraction, particularly affecting waters issuing along the western springline of the Sierra San Marcos. The desiccation of Laguna Grande after the 2008 sampling is a clear indicator of this. It is worth noting that our data plot slightly below that of Johannesson *et al*. (2004) and Rodriguez *et al*. (2005) (Fig. 3a) with a LEL slope of 4.5 as opposed to 4.9 and 5.15 respectively, indicating possible increasing PET in the basin. However, we recognize that the LEL slope change is small and could be a function of a number of climatic factors, including aridification, the origin of the vapour mass, seasonality of precipitation, evaporation during and after rainfall (Clark and Fritz, 1997).

Despite the observation that ground water levels have been declining, the lack of change in the range of water isotope composition between the previous studies (Johannesson *et al*. 2004; Rodriguez *et al*. 2005) and our study (Table 2), suggest the >60 yr residence time of aquifer water (Wolaver *et al*. 2013) may be dampening any atmospheric forced change in the surface water geochemistry particularly in the waters not subjected to surface evaporation (e.g. Poza Anteojo, Poza Churince, Poza Becerra). Conversely, high evaporation waters in the terminal east CCB are isotopically modified away from the source water (Fig. 3a). So although the basin overall might be considered to be naturally hydrologically closed, because of its complex internal hydrology, it doesn't behave like a classic closed basin e.g. Smith Creek (Thomas *et al*. 1989).

As such, the best areas for monitoring water loss and environmental degradation are between the low and high evaporation end members, possibly in the marsh in area W(b) (Fig. 2). Surface and subterranean flow in this part of the CCB is complex and as such the marsh system may be the most accurate representation of closed basin systematics and consequently, most reliable area for palaeoenvironmental study.

PET effects are evident in all three studies of the CCB surface waters and given the variability in data, vulnerability of the piedmont marsh system to environmental degradation, and socio-economic importance of the CCB, further study is certainly warranted to understand basin wide evaporative effects and potential for groundwater abstraction from the eastern flow system.

5. Conclusions

Isotope data ($\delta^{18}O$, δD and $\delta^{13}C_{TDIC}$) from this study suggest that apart from the drainage canal, the CCB is currently hydrologically closed, with different degrees of surface evaporation probably dependent on residence time in the basin. There is evidence for through-flow between water bodies as they become isotopically evolved due to evaporation. Groundwater discharge in the CCB appears to be a complex mix of hydrothermal groundwater probably originating from a regional aquifer; ambient meteoric karst water; and water originating from a deep lying karst reservoir. All the waters lie on a LEL with a slope of 4.5 indicating evaporation of surface waters is changing the isotopic composition of the CCB surface waters. Water body temperature data indicate that the observed evaporation of the CCB surface water is not related to the temperature of the water sampled, however, the data cohort is small. At least four separate hydrological systems have been identified based on the isotope data described here:

1) An independent system (Poza Anteojo), closely reflecting the isotopic composition of modern precipitation, is consistent with recharge in the Sierra Madera, previously suggested by Johannesson *et al*. (2004).

2) High temperature groundwater discharge on the western springline of the Sierra San Marcos (W(a)), flowing through the central ciénega area (W(b)) towards the terminal east of the basin (E(b)) (primary through-flow system).

3) Low water temperature, secondary through-flow system is evident on the eastern flank of the Sierra San Marcos y Pinos (area E(a)), suggesting a greater influence of meteoric karst waters.

4) Low water temperature endorheic system where hydrologic systems 2 and 3 (primary and secondary through-flow) terminate.

$\delta^{13}C_{TDIC}$ data suggest that the carbon in the CCB is sourced from both aquifer carbonate and soil derived CO_2.

Although based on a limited number of common samples, comparison of the isotopic data reported here with that of Johannesson *et al*. (2004) and Rodriguez *et al*. (2005) indicates that at sites where the residence time of the groundwater is long and/or the system is hydrologically open, $\delta^{18}O$ values may not be reliable indicators of water loss and therefore environmental degradation. Our data suggest the area W(b) is the most viable area for palaeoenvironmental study and long term monitoring is an essential tool in the identification of ecosystem damage and response, allowing for better future management of the complex and fragile CCB ecosystem.

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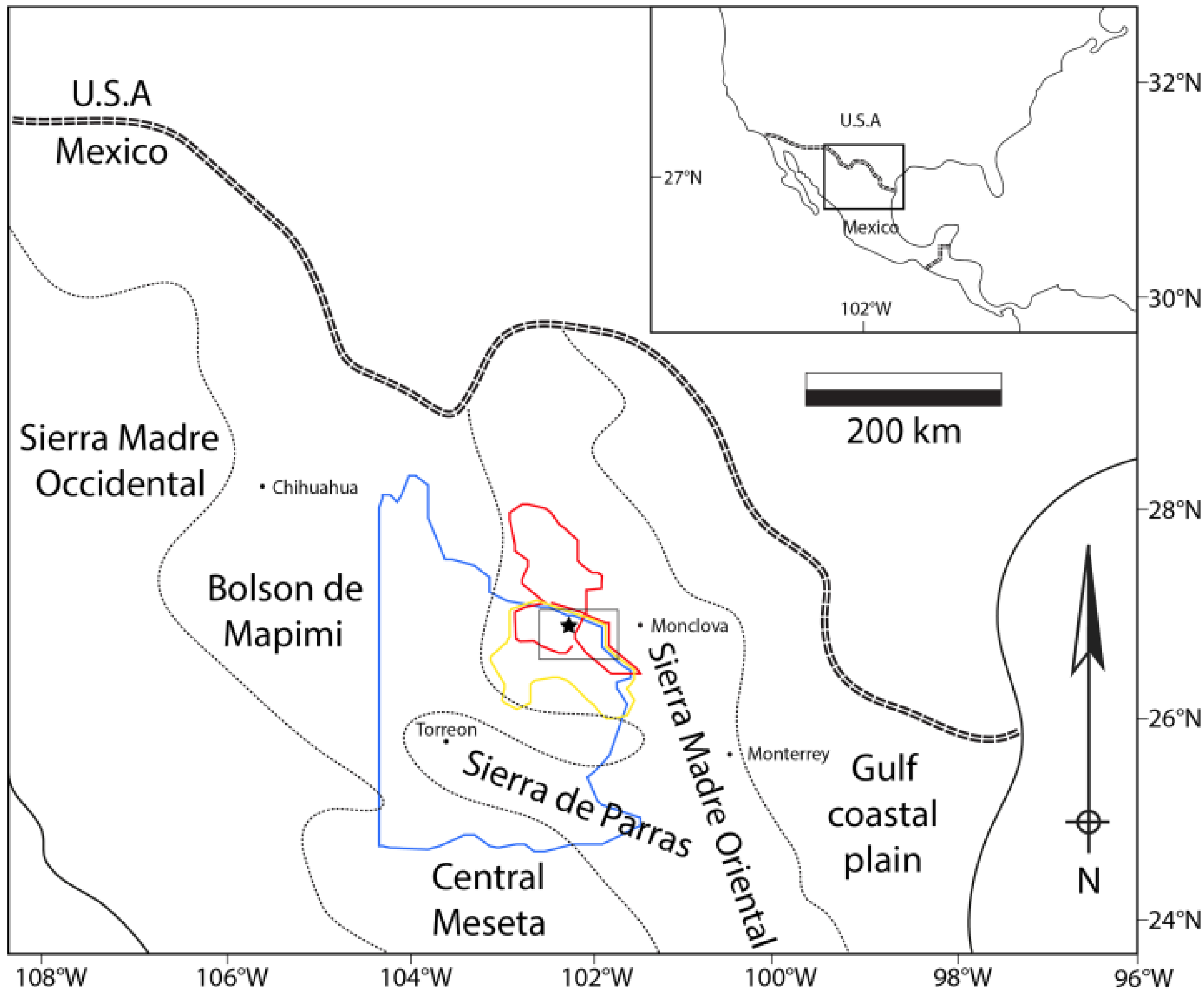

Figure 1: Location of the Cuatrociénegas Basin, NE Mexico. (a) Map shows regional geographic features, including the Sierra Madre Occidental, Bolson de Mapimi, Sierra de Parras, Sierra Madre Oriental and Gulf coastal plain. CCB groundwater catchments and recharge areas (see Wolaver *et al*. 2008) are also shown, including the Saca del Fuente, Santa Tecla Canal, and the Ocampo Valley local flow system (red line); Hundido, San Marcos and Sobaco Valleys (yellow line); and the 91,000 km^2 regional catchment area (blue line). Black star shows the location of Cuatro Ciénegas (base map from *GeoMapApp*, Ryan *et al*. 2009). **Colour reproduction on the Web only and black and white in print.**

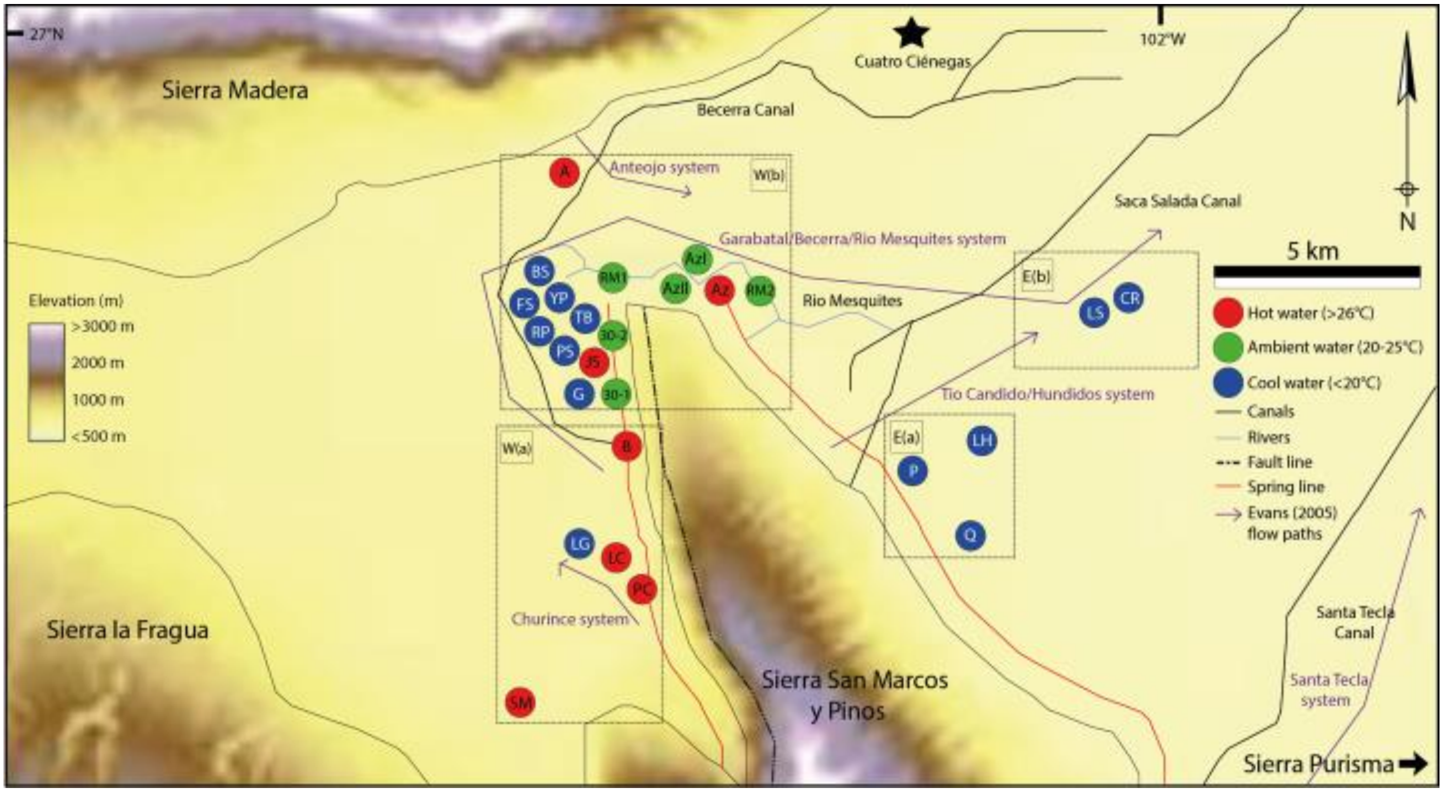

Figure 2: Water isotope sample locations, separated into four areas - W(a), W(b), E(a), E(b) - within the CCB. Sample codes are as follows: SM – San Marcos; PC – Poza Churince; LC – Laguna Churince; LG – Laguna Grande; B – Poza Becerra; G – Poza Garabatal; 30-1 – Mex 30-1; JS – Poza Juan Santos; PS – Palm Spring; RP – Rim Pond; FS – Fast Stream; TB – Poza Tierra Blanca; YP – Yucca Pond; BS - Bone Site; 30-2 – Mex 30-2; A – Poza Anteojo; RM1 – Rio Mesquites; AzII – Poza Azul II; Az I – Poza Azul I; Az – Poza Azul; RM2 – Rio Mesquites 2; Q – Poza Quintero; P – Poza Pronatura; LH – Los Hundidos; LS – Las Salinas; CR – Charco Rojo. **Colour reproduction on the Web only and black and white in print.**

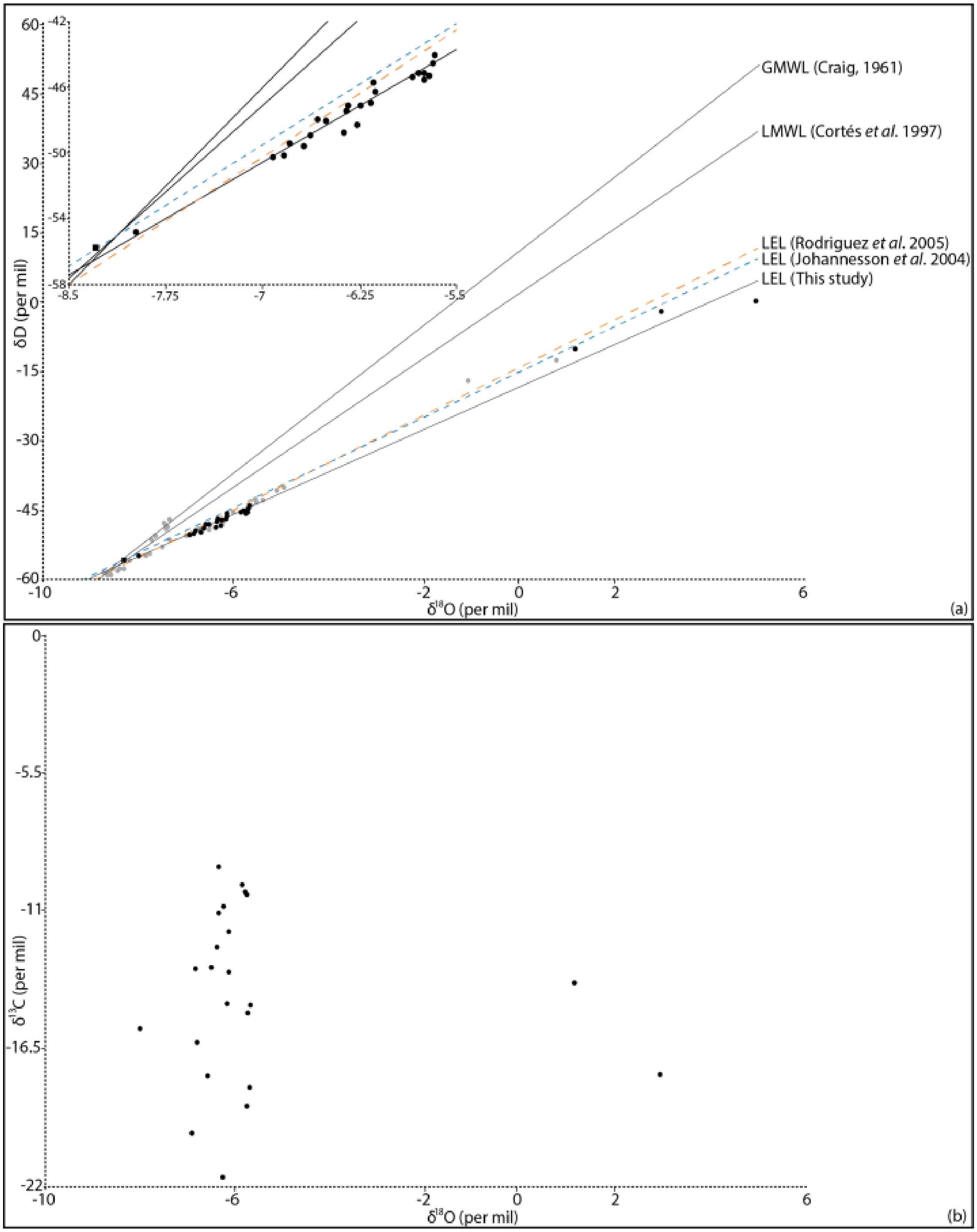

Figure 3: (a) $\delta^{18}O$ and δD data for waters sampled from the CCB. The GMWL (Craig, 1961) and LMWL (Cortés *et al*. 1997) are displayed with CCB residual water plotting to the right as a Local Evaporation Line (LEL) $\delta D = 4.5\delta^{18}O - 19$. LELs of $\delta D = 4.9\delta^{18}O - 15.1$ (blue line) and $\delta D = 5.15\delta^{18}O - 14.2$ (orange line) from Johannesson *et al*. (2004) and Rodirguez *et al*. (2005) respectively, are also shown. Grey dots represent CCB water samples from Rodriguez *et al*. (2005) for comparative purposes. The inset shows the main cluster of data points in more detail. Black square denotes seasonally weighted groundwater, indicative of precipitation (Wassenaar *et al*. 2009). (b) $\delta^{18}O$ and $\delta^{13}C_{TDIC}$ data for waters sampled from the CCB. **Colour reproduction on the Web only and black and white**